

Constrained equilibrium as a tool for characterization of deformable porous media.

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Abstract

A new method for characterizing the deformable porous materials with non-critical adsorption probes is proposed. The mechanism is based on a driving the adsorbate through a sequence of constrained equilibrium states with the insertion isotherms forming a pseudo-critical point or a van der Waals-type loop. In the framework of a perturbation theory and Monte Carlo simulations we have found a link between the loop parameters and the host morphology. This allows one to characterize porous matrices through analyzing a shift of the pseudo-critical point and a shape of the pseudo-spinodals.

I. INTRODUCTION

One of the methods for characterization of porous materials^{1,2} is a retrieving of pore size distributions through adsorption probes. Capillary condensation in macro- or mesopores permits to detect them rather reliably because the condensation pressure and temperature are very sensitive to the pore size. Nevertheless, it becomes more and more questionable³ that the true equilibrium behavior is observed in experiments. One of the major problems is a well developed metastability leading to very long equilibration times. Therefore, the condensation is usually detected as an onset of hysteresis. Nevertheless, it has recently been argued⁴ that the hysteretic behavior is not necessarily associated

with an underlying equilibrium phase transition. In the case of micro-pores the situation is even more difficult because such pores are too small to support any sharp (bulk-like) phase transition. This makes one to search for alternative characterization mechanisms which are not based on the critical behavior. In the case of deformable matrices⁵, such as aerogels^{6,7} or amorphous intercalation compounds⁸, the problem is additionally complicated by variations of the host morphology with the guest density or pressure. Thus the guest response (e.g., adsorption isotherms) is a superposition of at least two contributions - the adsorbate thermodynamics under the host confinement and the adsorbate-induced host deformation.

In this paper we propose a method for a pore size determination through adsorption of non-critical fluids. The main idea is to find an explicit relation between the density-dependent matrix morphology and some peculiarity in the fluid thermodynamic response. The mechanism is based on our finding⁹ of negative compressibility states in confined dilatating systems. These states can appear as a consequence of a driving path - either a sequence of controlled lateral dilatations⁹ or a sequential adsorption of prescribed portions¹⁰. This imposes an additional constraint¹¹ on the fluid equilibrium. As a result, at certain conditions one can observe a sequence of states which form a van der Waals-type loop in the isotherm. Then the loop parameters can be taken as the required specificities for a detection of the confining geometry.

II. MODEL

The matrix is considered as a collection of slit-like pores with different widths h_i distributed according to some probability density. For simplicity the pores are assumed to be uncorrelated. This allows us to focus on a single pore of fluctuating width h and surface area S . The width is known only statistically, that is, from a probability distribution $f(h)$. The slit itself is a part of the hosting system, whose coupling to the guest species changes the slit geometry (see below). The fluid is modeled as N hard spheres of diameter $\sigma = 1$, injected into the pore. The hard core potential allows us to

mimic the excluded volume effects and ensures that the fluid is off-critical (we do not consider freezing-type transitions).

For any h the total Hamiltonian is

$$H = H_{ff} + H_{fw}, \quad (1)$$

where H_{ff} is the hard sphere Hamiltonian, H_{fw} is the slit potential

$$H_{fw} = A \sum_{i=1}^N \left[\frac{1}{z_i^k} + \frac{1}{(h - z_i)^k} \right]; \quad 1/2 \leq z_i \leq h - 1/2. \quad (2)$$

We do not take into account a short-ranged fluid-wall attraction, responsible for the surface adsorption or layering effects. The inverse-power shape for H_{fw} is chosen as a generic form of a soft repulsion, with k controlling the softness. In some sense this mimics the hydrophobic or non-wetting effects that, as we will see later, are essential. On the other hand, this simple model takes into account that the walls are impenetrable and ignores possible localized adsorption effects, which could complicate the overall picture. For technical purposes we are working with $k = 3$. Moreover, our results are qualitatively insensitive to a particular choice of k .

In principle, one may consider two adsorption mechanisms. One is an equilibrium between the pore and the bulk fluids. In that case N would change according to the chemical potential $\mu = \mu_b$. In this paper we treat another mechanism. Namely, an adsorption in doses¹⁰, when N is injected in prescribed portions. In that case we have a sequence of the fluid equilibrium states corresponding to different N . The sequence is determined by an injection procedure, which imposes an additional constraint. It should be emphasized that choosing the model we tried to retain only a minimal number of relevant ingredients: the absence of liquid-gas transition in the fluid bulk, excluded volume effects, and a density-dependent heterogeneous confinement.

III. PERTURBATION THEORY

A. Conditional insertion isotherm

At any pore width h the free energy can be represented as

$$\beta F(h) = \beta F_0(h) - \ln \langle e^{-\beta H_{fw}} \rangle_0 \quad (3)$$

where $F_0(h)$ is the free energy of a reference system, and $\langle \dots \rangle_0$ is the average over the reference state. Taking a spatially confined hard sphere system (the one with $A = 0$) as a reference, we consider a first order perturbation⁹ for the conditional free energy

$$\beta F(h) = \beta F_0(h) + \beta S \rho(h) \int \prod_i dz_i H_{fw} \quad (4)$$

where $\beta = 1/(kT)$ and $\rho(h)$ is the pore density in the "slab" approximation

$$\rho(h) = \frac{N}{S(h-1)}, \quad (5)$$

ignoring a non-monotonic behavior of the density profile with increasing pore density. This is reasonable for wide pores and low fluid densities. The reference part is estimated in the excluded volume approximation, while the perturbation contribution is $N\Psi(h)$, such that the total conditional free energy is

$$\beta F(h) = -N \ln \left[\frac{1 - b\rho(h)}{\Lambda_T^3 \rho(h)} \right] - N + N\beta\Psi(h) \quad (6)$$

where $b = 2\pi\sigma^3/3$ is the excluded volume factor, Λ_T is the thermal de Broglie length and

$$\Psi(h) = 16A \frac{h}{(1-2h)^2} \quad (7)$$

The conditional insertion isotherm can be calculated in the standard way

$$\beta\mu(h) = \left(\frac{\partial \beta F(h)}{\partial N} \right)_{\beta, S, h} = \ln \left[\frac{\Lambda_T^3 \rho(h)}{1 - b\rho(h)} \right] + \frac{b\rho(h)}{1 - b\rho(h)} + \beta\Psi(h) \quad (8)$$

which relates the fluid density $\rho(h)$ and the chemical potential $\mu(h)$.

B. Matrix dilatation

As is discussed above, the pore dilatation can be taken into account, assuming that the width h is density-dependent. Real insertion materials are usually rather complex (multicomponent and heterogeneous). For that reason one usually deals with a distribution of pore sizes or with an average size. In this context we assume that h is known only

statistically and the probability distribution $f(h|\rho)$ is conditional⁹ to the guest density ρ , which should be selfconsistently found from

$$\rho = \int dh f(h|\rho) \rho(h). \quad (9)$$

This relation reflects an injection sequence $\rho(h)$ and the matrix dilatation. Note that the average density ρ is not uniquely determined by the particles insertion but is also conditional to the matrix response. Namely this constraint makes the problem non-trivial, inducing a coupling between the insertion and the dilatation modes. Taking our result for $\mu(h)$, we can focus on the insertion isotherm, averaged over the width fluctuations.

$$\mu(\rho) = \int dh f(h|\rho) \mu(h). \quad (10)$$

This, however, requires a knowledge on the distribution $f(h|\rho)$. Even without resorting to a concrete form for $f(h|\rho)$, it is clear that the matrix reaction can be manifested as a change in the distribution width or/and the mean value. One of the simplest forms reflecting at least one of these features is a δ -like distribution, ignoring a non-zero width:

$$f(h|\rho) = \delta[h - h(\rho)], \quad (11)$$

where $\delta(x)$ is the Dirac δ -function and the mean pore width $h(\rho)$ is density-dependent. For concreteness we consider the swelling behavior⁸. Therefore, the mean pore width $h(\rho)$ increases with ρ . For illustration purposes we take the *S*-shaped form, considered previously^{5,9}

$$h(\rho) = h_0(1 + \tanh[\Delta(\rho - \rho_0)] + \tanh[\Delta\rho_0]). \quad (12)$$

This form resembles a non-Vegard behavior, typical for layered intercalation compounds⁵. The dilatation is weak at low densities ($\rho \ll \rho_0$), the most intensive response is at $\rho \approx \rho_0$, and then the pore reaches a saturation, corresponding to its mechanical stability limit. Here Δ is the matrix response constant or dilatation rate, controlling the slope near $\rho \approx \rho_0$, and h_0 is the mean pore width in the absence of insertion. This should be considered as a generic form that samples a non-linear increase of the average pore width,

resolved at a given density ρ . The model mimics certain heterogeneity aspects which, as we believe, are essential. On the other hand, this choice allows us to map the problem in question onto the negative compressibility problem⁹ in systems with fluctuating geometry.

From eq. (9) the average density is found to be

$$\rho = \frac{N}{S} \frac{1}{h(\rho) - 1} \quad (13)$$

Changing the surface density N/S (by increments in N) we vary the average pore density ρ . This allows us to eliminate N/S in the favor of ρ in all thermodynamic functions. Combining eqs (8), (9) and (10) we obtain

$$\beta\mu(\rho) = \ln \left[\frac{\Lambda_T^3 \rho}{1 - b\rho} \right] + \frac{b\rho}{1 - b\rho} + 16\beta A \frac{h(\rho)}{(1 - 2h(\rho))^2} \quad (14)$$

In the case of wide pores and a weak dilatation we expand $\beta\mu$ in terms of $1/h_0$ and Δ , obtaining a generic van der Waals form

$$\beta\mu(\rho) = \ln \left[\frac{\Lambda_T^3 \rho}{1 - b\rho} \right] + \frac{b\rho}{1 - b\rho} + \frac{4\beta A}{h_0} - \frac{12\beta A}{h_0} \rho \Delta \quad (15)$$

Therefore, as in the previous study⁹, we have an interplay of several effects – the packing (first two terms), the fluid-matrix interaction (density-independent), and the dilatation (linear in density). It is seen that a coupling of the fluid-slit repulsion (A), spatial confinement (h_0) and the dilatation (Δ) acts as an effective infinite-range fluid-fluid attraction. The latter induces an inflection point (or even a loop) in the isotherm $\mu(\rho)$. Introducing a dimensionless temperature $T^* = 1/(4A^*)$, and solving

$$\frac{\partial(\beta\mu)}{\partial\rho} = 0; \quad \frac{\partial^2(\beta\mu)}{\partial\rho^2} = 0 \quad (16)$$

we find the pseudo-critical parameters at which the inflection point appears.

$$\rho_c = \frac{1}{3b}; \quad T_c^* = \frac{4}{27} \frac{\Delta}{bh_0} \quad (17)$$

Plugging these back into eq. (14) we get the third parameter $\mu_c = \mu_c(b, h_0, \Delta)$.

As has already been mentioned, the loop is not a signature of a phase transition. It is a sequence of equilibrium states, constrained by a coupling between the insertion and the

dilatation modes. The physical mechanism is quite similar to the previously reported⁹. We deal with a competition of two effects: the interparticle and wall-particle repulsions tend to increase the insertion energetic cost μ with increasing ρ , while the pore dilatation diminishes it. As a result, at certain parameters the isotherm becomes nonmonotonic. For a purely attractive pore ($A < 0$) the inflection point does not appear. Therefore, the wall-particle repulsion is an essential ingredient. This suggests that a suitable combination of the repulsive and attractive parts is a criterium for choosing the adsorption probe. As it should be, the inflection (loop) feature disappears in the bulk limit $h_0 \rightarrow \infty$ or in the case of rigid matrices $\Delta \rightarrow 0$.

In order to improve the accuracy of the theoretical results, the reference part is replaced by the Carnahan-Starling form

$$\beta\mu = \ln(\rho\Lambda_T^3) + \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} + 16\beta A \frac{h(\rho)}{(1-2h(\rho))^2}; \quad \eta = \pi\rho/6. \quad (18)$$

This allows us to avoid the unphysical behavior at high densities and escape from the flaws of the excluded volume approximation (14). In particular, all the pseudo-critical parameters (ρ_c, T_c^*, μ_c) appear to be related to the parameters of the pore width distribution (h_0, ρ_0, Δ) . Therefore, driving the system close to the pseudo-critical point permits to estimate the density dependent pore size distribution.

IV. SIMULATION

In order to verify the existence of the loop predicted by the perturbation theory as well as to test the accuracy of the theoretical estimation, the simulation of the model in question has been carried out applying the Widom test particle insertion method¹². As in our previous work⁹ we applied the conventional canonical *NVT* MC simulations of a confined hard sphere fluid. The simulation cell was parallelepiped in shape, with parallel walls at surface separation h , and constant surface area $S = L_x \times L_y = 12 \times 12$. The periodic boundary conditions were applied to the X and Y directions of the simulation box; the box length in the Z direction is fixed by the pore width. For a given pore

width the adsorbed fluid density is chosen according to the Eq.(5) varying the number of particles, N . At frequent intervals during this simulation, a coordinate \mathbf{r}_{N+1} has been generated randomly and uniformly over the simulation cell. For this value of \mathbf{r}_{N+1} , we have computed $\langle \exp(-\beta H(\mathbf{r}_{N+1})) \rangle_N$ averaged over all generated trial positions. In such a manner the chemical potential of the system with density ρ has been calculated,

$$\beta\mu = -\ln \left[\frac{\rho}{\langle \exp(-\beta H(\mathbf{r}_{N+1})) \rangle_N} \right], \quad (19)$$

where H is the system Hamiltonian.

Each simulation runs 4×10^5 MC cycles, whith the first half for the system to reach equilibrium whereas the second half for evaluating the ensemble averages.

V. RESULTS

Adsorption isotherms are plotted in Figure 1. It is seen that the inflection point around $\rho \approx 0.3$ transforms into the loop with increasing repulsion A (or decreasing temperature T^*). As expected⁹, the perturbation theory underestimates the magnitude of A at which these effects appear. The loop gets sharper with increasing dilatation rate Δ and becomes more pronounced with decreasing pore width h_0 . It is remarkable that the fitting on the pseudo-critical (inflection) point (part (a)) or on the loop (part (b)) allows us to find the set of the distribution parameters (h_0, Δ, ρ_0) in a perfect agreement with the simulation. Attempts to fit under other criteria (e.g. the least-square deviations) give incorrect values of these parameters.

In agreement with our theoretical prediction (17), the simulation results confirm that the pseudo-critical point (and the loop) is reachable at any appropriate choice of the model parameters. This is in contrast to what was reported⁹ for the negative compressibility states in the same model with lateral stretching (increasing S while N is fixed). There the loop has been found to appear only if the slit reaction Δ reaches some threshold value Δ^* which involves a combination of h_0, ρ_0 and A . In other words, the variation of the average density ρ due to the transversal dilatation should dominate its variation, induced by the

changes in the surface density N/S due to the lateral stretch. This difference suggests that the driving path (namely, changing the fluid density by a lateral stretch or by a particle injection) is really important for this sort of systems. On the other hand, in the context of the present study, the fact that the pseudo-critical parameters do not involve any additional condition, is quite favorable for making a link between these parameters and the matrix morphology.

In Figure 2 the pseudo-critical parameters are analyzed. It is seen that ρ_c grows with the dilatation rate Δ almost linearly exhibiting a characteristic kink. The latter signals a crossover from a weak to a strong dilatation regime. The kink shifts to lower Δ and becomes less pronounced with decreasing h_0 (that is why it is almost undetectable for $h_0 = 5$). At low Δ the pseudo-critical density is practically independent of h_0 , while at high Δ it approaches ρ_0 . In agreement with our simplified estimation (17), $T_c^*(\Delta)$ can be reasonably approximated by a straight line (the lower inset). Nevertheless, it exhibits a weak inflection point at the same Δ (around $\Delta = 4$) as ρ_c does. The pseudo-critical temperature increases with decreasing h_0 . This is also coherent with the estimation (17) predicting a decrease in the slope inversely proportional to h_0 . In contrast, the insertion energy μ_c decreases and becomes insensitive to h_0 with increasing Δ (the upper inset). This agrees well with the physical intuition that the pore dilatation diminishes an overlap between the repulsive wall fields, making the insertion less energetically consuming.

In practice, an exact capture of the inflection point could be too demanding. Driving at rather low temperatures ($T < T_c^*$), such that the system develops the loop, should be much easier. In that case a shape of the pseudo-spinodals could also be used as an indicator of the matrix morphology. These curves are plotted in Figure 3. It is seen that the pseudo-spinodals become broader with decreasing dilatation rate and shift to higher ρ with increasing Δ . Comparing this with the previous figure, we can see again that ρ_c converges to ρ_0 with increasing dilatation rate Δ . If necessary, other quantitative characteristics, such as the curve asymmetry with respect to ρ_c or μ values at the spinodal points, can also be easily extracted.

These results illustrate a correlation between the pseudo-critical point (or the loop)

parameters and the density-dependent pore geometry. We did not try to obtain these parameters from the simulation because the procedure is time consuming, while new physical insights, compared to the analytical estimations, are difficult to expect. The only promising point is to consider narrow ($1 \leq h_0 \leq 2$) pores, for which the first-order perturbative scheme could fail even qualitatively. This point is left for a future analysis.

VI. DISCUSSION AND CONCLUSION

A method for characterizing the deformable porous materials by adsorption of non-critical fluids is proposed. It is based on a driving the host-guest system through a sequence of constrained equilibrium states, forming a loop in the insertion isotherms. The constraint appears from a coupling of the insertion and the matrix dilatation modes, inducing a competition between the repulsive interactions and their relaxation by the host dilatation. As a result the insertion isotherms develop pseudo-critical points or loops, whose parameters are shown to be correlated with the parameters of the pore size distribution. In particular, we have found that the magnitudes of the geometrical parameters (h_0 , ρ_0 , Δ) which reproduce well the inflection point or the loop, perfectly agree with their values in the simulation. This suggests that the peculiar points (with $\partial\mu/\partial\rho = 0$ or $\partial\rho/\partial\mu = 0$) are extremely sensitive to the matrix morphology, while the overall isotherm shape is less important (unless one can achieve an exact isotherm coincidence). This is coherent with the recent finding¹³ that a matching of the inflection points (with $\partial\rho/\partial\mu = 0$) correctly reproduces the remaining part of the experimental isotherm. From the information-theoretical point of view¹⁴ such a criterium (the inflection matching) corresponds to a maximal amount of information one can get from a fitting of a model to a given experimental or simulation result. In our case we deal with the pseudo-critical point ($\partial\mu/\partial\rho = 0$). Fitting on this peculiarity corresponds to a singular information rate¹⁴, that allows us to update the geometrical parameters from their initial estimation in a limited range of ρ (around the singularity). Namely this type of singularity is used to characterize porous media¹ through a shift of the fluid condensation or freezing

point.

Although we have taken a simplified δ -like distribution, our conclusion should hold in general because the characteristic loop feature is directly related to the dilatation mode. The latter translates into a shift of the mean pore size, that has been taken into account. Nevertheless, the role of a non-zero distribution width remains to be investigated. The only restriction is that the number of the detected loop parameters should be (at least) equal to the number of parameters determining the pore size distribution. This restriction is not too strong because in practice the distribution is usually characterized by only few parameters (e.g. leading mean pore sizes and dispersions around them). On the other hand, the proposed method is mainly intended for a complementary detection of the porosity range (e.g. micropores) where other techniques fail. For illustration and technical purposes we were working with rather large pores $10 \leq h(\rho) \leq 30$. This, however, does not affect our main concept.

It should be emphasized that, since we deal with a constrained equilibrium, the loop does not violate the thermodynamic stability¹¹. Therefore, this feature can be readily found under suitable experimental conditions, similar to those realized in the low-pressure adsorption into microporous matrices¹⁰. In this respect it is worth noting that quite similar loop features have been detected¹⁰ for nitrogen and argon adsorption in microporous carbons and synthetic zeolites. As in our case, the fluids have been inserted in sequential doses. Nevertheless, in contrast to our assumption, there is no evidence for an insertion-induced dilatation of these slit-shaped materials. The loops have been interpreted as a signature of a monolayer-induced micropore filling¹⁰. In this context we can propose an alternative interpretation of our results, making a link to the experimental observations. Namely, it is well known¹⁰ that the micropore filling starts from the narrowest pores (h_0 in our language). As the fluid pressure (or density) increases, the larger micropores progressively fill. Microscopically this effect appears from an interplay of repulsive and attractive parts of the wall-particle interaction. The latter depends on the chemical nature of the probe and the matrix geometry and composition. In order to extract general features, one may accept this effect as an experimental fact, trying to see its consequences.

Therefore, in a given density domain the fluid resolves a quite narrow range of pore sizes because the narrow pores are already blocked by a preceding dose, but the filling of larger pores is not thermodynamically favorable at this density. This fact is captured by our distribution $f(h|\rho)$ that can be re-interpreted as an effective density-dependend matrix heterogeneity, with Δ being the heterogeneity index. In other words, an increase of the mean pore size $h(\rho)$ may result from a pore blocking effect. This interpretation is coherent with the one proposed by the authors of¹⁰, who claimed that the S-shaped feature (the loop) signals a switching from the ultramicropore to micropore filling. Nevertheless, this qualitative analogy between the matrix swelling and heterogeneity requires further analysis, including a competition of the repulsive and attractive interactions. This issue is left for a future study.

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FIGURES

FIG. 1. Insertion isotherms for a weakly (a) and strongly (b) repulsive slit. The other parameters are $h_0 = 10$, $\Delta = 15$, $\rho_0 = 0.3$ (both theory and simulation)

FIG. 2. Variation of the pseudo-critical parameters with the dilatation rate Δ . $\rho_0 = 0.3$, $h_0 = 5$ -squares, $h_0 = 10$ -circles

FIG. 3. Pseudo-spinodal curves at different dilatation rates Δ . The other parameters are $h_0 = 7$, $\rho_0 = 0.3$

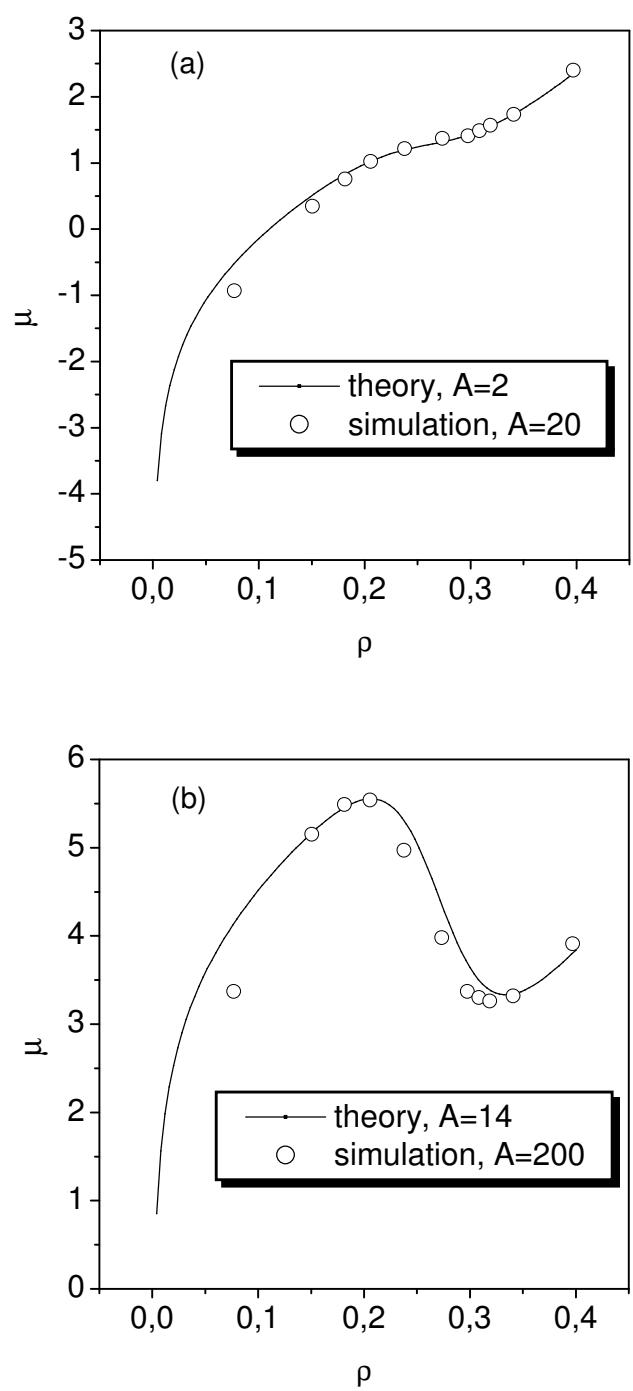


Figure 1

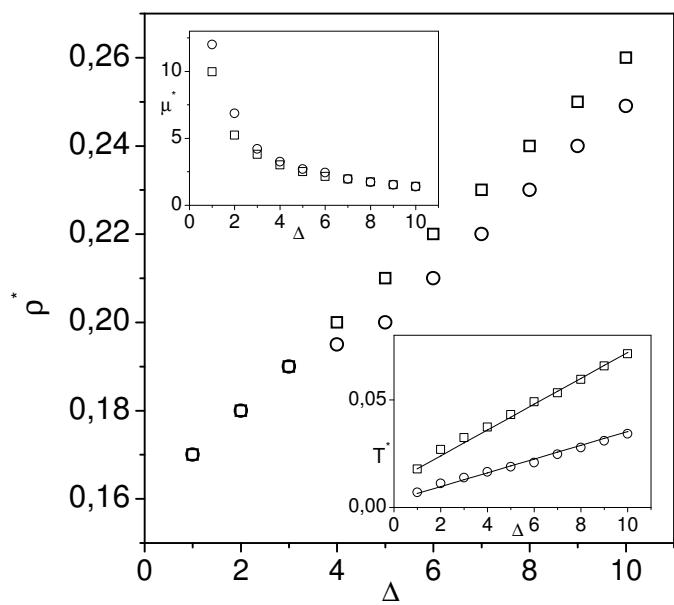


Figure 2

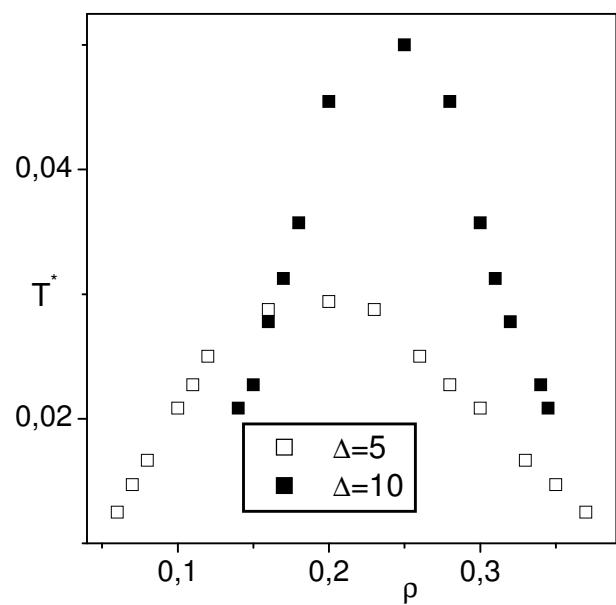


Figure 3